

# MERCURY REMOVAL FROM COMBUSTION FLUE GAS BY ACTIVATED CARBON INJECTION: MASS TRANSFER EFFECTS

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## INTRODUCTION

The Clean Air Act Amendments of 1990 listed 189 substances as hazardous air pollutants, of which 37 substances have been detected in power plant emissions. Of the 37 hazardous air pollutants, 11 are trace metal species. Mercury is trace metal species of greatest concern because of perceived risks from its environmental release and because it is present mainly in the vapor form and is not captured effectively by existing particulate removal systems.

Carbon-based processes (both direct injection and fixed-bed) have been developed for control of mercury emission from municipal- and hazardous-waste incinerators. Existing data from the incinerators provide some insight on mercury control, but these data cannot be used directly for coal-fired utilities because mercury concentration, species, and process conditions differ greatly<sup>1</sup>. For example, municipal solid waste (MSW) mercury concentrations (200 to 1000  $\mu\text{g}/\text{m}^3$ ) are one to two orders of magnitude higher than for coal combustion sources which contains typically 5 to 10  $\mu\text{g}/\text{m}^3$ .

Injection of activated carbon upstream of a particulate control has the potential of providing a low-cost option for control of mercury emissions from utility flue gas<sup>1</sup>. In several bench<sup>2-7</sup> pilot and full-scale tests<sup>8-10</sup> of the method, the influence of carbon type<sup>2-4,10</sup>, carbon structure<sup>3-4</sup> and carbon surface chemistry<sup>2,4,5,7</sup>, injection methods (dry or wet)<sup>10</sup>, amount of carbon injected<sup>8-10</sup>, and flue gas temperatures<sup>8-10</sup> on mercury removal have been examined. The low concentrations of mercury in the flue gas, and limited exposure time (3 seconds) of the sorbent, generally required large amounts of activated carbons in these sorbent injection tests. To achieve high Hg removal (>90%), the required ratio of carbon to mercury (C/Hg) in the flue gas has generally (on weight basis) been found to be 3,000-20,000, depending on the process conditions. Tests have shown that the carbon to mercury ratio in MSW incinerators is more than an order of magnitude lower than that necessary to achieve similar mercury removal in coal combustors.

The high C/Hg ratio could be a result of either mass transfer limitation or low mercury capacity of carbon due to the extremely low concentration of mercury in the flue gas, or the low reactivity of the carbon. To reduce the operating cost of the carbon injection process, either a more efficient sorbent that can operate at a lower C/Hg ratio, or a lower-cost sorbent, or both is required. An understanding of physical and chemical processes that affects mercury removal from flue gas and a systematic sorbent development study would be required to develop an efficient, cost effective carbon injection process for removal of mercury from coal-fired utility flue gas.

The work presented here represents phase I of an ongoing EPRI and Illinois Clean Coal Institute funded research program to develop a low-cost, high efficiency sorbent for mercury removal. In this paper the influence of both film and intraparticle mass transfer on mercury removal in the carbon injection process are described.

## MASS TRANSFER CALCULATIONS

### Film Mass Transfer.

In absence of internal (intraparticle) diffusion, the equation describing the transfer of mercury molecules from the bulk flue gas to the surface of carbon per unit interfacial area is:

$$N = k_g (C_g - C^*) \quad (1)$$

where  $N$ =mass flux ( $\text{g}/\text{cm}^2\text{s}$ );  $k_g$  is mass transfer coefficient ( $\text{cm}/\text{s}$ );  $C_g$  are the mercury concentration ( $\text{g}/\text{cm}^3$ ) in the bulk flue gas and  $C^*$  is the mercury concentration in equilibrium with the adsorbed mercury on the carbon surface. Assuming the interfacial area per unit volume in the duct is  $a/V$ , the flux per volume of the duct will be:

$$N = k_g \frac{a}{V} (C_g - C^*) \quad (2)$$

where  $a$  is the total interfacial area in the duct ( $\text{cm}^2/\text{cm}^3$ ) and  $V$  is the total volume of the duct ( $\text{cm}^3$ ) and  $C_g - C^*$  is considered as the driving force for mass transfer.

The typical mercury concentration in the utility flue gas is about 10  $\mu\text{g}/\text{Nm}^3$  and usually 90% removal is required. Typically, the particle size of powdered activated carbon ranges between 1 and

60  $\mu\text{m}$ . When injected into the flue gas, the fine carbon particles will suspend and flow with the gas stream. The relative velocity between the particles and the flue gas is practically zero. If the carbon particles are well dispersed and do not agglomerate during the process, the mass transfer coefficient at the gas-solid interface could be calculated by the following equation:

$$\frac{k_g d_p}{D_{Hg}} = 2 \quad (3)$$

where  $d_p$  = particle size (cm) and  $D_{Hg}$  = diffusivity of the mercury molecule in flue gas ( $\text{cm}^2/\text{s}$ ). Equation (3) shows that the mass transfer coefficient  $k_g$  increases with decreasing carbon particle size. Any attempts to introduce turbulence to the flow may not have any significant effects on the mass transfer coefficient.

The value reported in the literature for the diffusivity of mercury in air at  $341^\circ\text{C}$  is  $D_{Hg} = 0.473 \text{ cm}^2/\text{s}$  which can be corrected to the flue gas temperature ( $140^\circ\text{C}$ ),  $D_{Hg} = 0.261 \text{ (cm}^2/\text{s)}$ . Substituting this value into equation (3) gives :

$$k_g = \frac{2D_{Hg}}{d_p} = \frac{2 \times 0.261}{d_p} = \frac{0.522}{d_p} \text{ (cm/s)} \quad (4)$$

If no strong turbulence or back mixing occurs in the duct, the gas-solid phase can be modeled as a plug flow system. The mass balance equation for a plug flow system is:

$$k_g \frac{a}{V} (C_g^* - C_g) S dz = -F_g dC_g \quad (5)$$

where  $S$  is the cross section area of the duct ( $\text{cm}^2$ ),  $F_g$  is the flue gas flow rate ( $\text{Nm}^3/\text{s}$ ) and  $dz$  is the differential length of the duct (cm).

To examine the role of film mass transfer (the maximum mass transfer flux), assume  $C^* \ll C_g$  at all positions in the duct (this means that mercury adsorption capacity of the carbon and the carbon reactivity are not limiting the mass transfer rate). Equation (6) is obtained by integrating equation (5) using the following boundary conditions:

At the entrance:  $z=0$ ,  $C_g=C_0$

At the outlet:  $z=L$ ,  $C_g=C_g$

$$\ln\left(\frac{C_0}{C_g}\right) = k_g \frac{a}{V} \frac{SL}{F_g} \quad (6)$$

where  $L$  is the length (cm) of the duct and  $SL/F_g = t$  is the residence time of carbon particles in the duct. For 90% mercury removal,  $C_g = 0.1C_0$  and Equation (6) can be rearranged to solve for the minimum interfacial area:

$$\frac{a}{V} = \frac{2.303}{k_g} \frac{F_g}{SL} = \frac{2.303}{0.522} \frac{d_p}{t} = 4.412 \frac{d_p}{t} \text{ (cm}^2/\text{cm}^3\text{)} \quad (7)$$

This relationship provides the minimum activated carbon interfacial area required by film mass transfer to remove 90% of the mercury from one  $\text{Nm}^3$  of utility flue gas.

Because only the external surface area of carbon particles serves as the gas-solid interfacial area the minimum interfacial area needed for mass transfer implies that a certain minimum amount of carbon is required to achieve the desired mercury removal. The minimum amount of carbon and thus the minimum ratio of carbon/mercury can be calculated as follows.

For spherical particles the external surface area per gram of activated carbon is:

$$\frac{\pi d_p^2}{\frac{1}{6} \pi d_p^3 \rho_c} = \frac{6}{d_p \rho_c} \quad (8)$$

where  $\rho_c$  is the carbon particle density in g/cm<sup>3</sup>. The amount of carbon required for mercury removal from one Nm<sup>3</sup> of utility flue gas therefore is:

$$(4.412 \frac{d_p}{t}) (\frac{6}{d_p \rho_c}) = 0.7353 \frac{d_p^2 \rho_c}{t} \quad (9)$$

The carbon /mercury ratio can be calculated from the following relationship:

$$\frac{\text{Carbon}}{\text{Mercury}} = 0.7353 \frac{\rho_c d_p^2}{t (C_o - C_g)} \quad (10)$$

Assuming carbon particle size of 10  $\mu\text{m}$ , residence time of 3 seconds, carbon particle density of 0.5 g/cm<sup>3</sup>, inlet mercury concentration of 10  $\mu\text{g}/\text{Nm}^3$ , and outlet mercury concentration of 1  $\mu\text{g}/\text{Nm}^3$ , the carbon/mercury ratio is:

$$\frac{\text{Carbon}}{\text{Mercury}} = 0.7353 \times \frac{0.5 \times (10 \times 10^{-4})^2}{3 \times (10 \times 10^{-12} - 1 \times 10^{-12})} = 13611$$

This analysis indicates that a high C/Hg ratio is required when the carbon particle size is larger than 10  $\mu\text{m}$ .

Equation (10) shows that the C/Hg ratio depends strongly on the particle size. Table 1 represents the carbon/mercury ratios required for 90% mercury removal under mass transfer limited conditions with activated carbon ranging in size from 1 to 10  $\mu\text{m}$  (particle density of activated carbon  $\rho_c = 0.5 \text{ g}/\text{cm}^3$  and contact time of 3 seconds were used).

Table 1 Carbon/mercury ratios for different carbon particle sizes

Particle size ( $\mu\text{m}$ )	$k_g$ (cm/s)	Interfacial area (m <sup>2</sup> /g)	Ratio of C/Hg *	
			Utility Flue Gas	MSW Flue Gas
10	522	1.2	13611	227
5.5	949	2.18	4117	68
5	1044	2.4	3402	57
3	1740	4.0	1224	20
1	5220	12.0	136	2.3

\* The inlet mercury concentrations for utility flue gas and MSW flue gas are 10 and 600  $\mu\text{g}/\text{Nm}^3$ , respectively.

Equation (10) also shows that the C/Hg ratio depends on the mercury concentration in the flue gas ( $C_o - C_g$ ). Usually, MSW incinerator flue gas has a mercury concentration of around 200-1000  $\mu\text{g}/\text{Nm}^3$  which is almost two orders of magnitude higher than that of utility flue gas. The C/Hg ratio, according to equation (10), for the MSW flue gas will be about two orders of magnitude lower than that of the utility flue gas. The last column of Table 1 lists the C/Hg ratios required for MSW flue gas. For example, the theoretical C/Hg ratio required for a MSW flue gas containing 600  $\mu\text{g}/\text{Nm}^3$  mercury is about 60 times lower than that of a utility flue gas containing 10  $\mu\text{g}/\text{Nm}^3$  mercury for the same level of mercury removal.

These calculated C/Hg ratios are the minimum needed and assumes mass transfer limitations. At low C/Hg ratios (such as for the MSW flue gas at a C/Hg ratio of 2.3), it is possible that the carbon will actually have reached its equilibrium capacity. Also at higher temperatures, most sorbents have very low capacity for mercury. Under these conditions much more sorbent than that predicted by mass transfer limitation will be needed.

#### Intraparticle Diffusion

Because diffusivities in microporous materials vary broadly, depending on the pore structure and pore size, it is difficult to estimate diffusivity when the diffusion is in the configurational range. Configurational diffusion only occurs when the micropore size is comparable to the molecular size of the adsorbate. In this study, calculations were made for a single spherical carbon particle dispersed in a flue gas. The carbon particle is exposed to a step change in mercury concentration at its external surface at  $t = 0$  (corresponding to the injection location). The diffusion of mercury molecules into the carbon, assuming a constant effective diffusivity, can be described by:

$$\frac{\partial q}{\partial t} = D_{Hg} \left( \frac{\partial^2 q}{\partial r^2} + \frac{2}{r} \frac{\partial q}{\partial r} \right) \quad (11)$$

where  $D_{Hg}$  is the mercury effective diffusivity in carbon particle and  $q(r,t)$  is the adsorbed phase concentration of mercury at position  $r$  (inside the carbon particle) and time  $t$ . If the mercury concentration at the external surface of the particle remains constant, the following initial and boundary conditions apply:

$$q(r_c, \frac{1}{2}d_p, t) = q_0 \quad (12)$$

$$q(r, 0) = 0, \quad (13)$$

$$\left( \frac{\partial q}{\partial r} \right)_{r=0} = 0 \quad (14)$$

The solution to this problem is given by<sup>(11)</sup>:

$$\frac{\bar{q}}{q_0} = \frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{4n^2\pi^2 D_{Hg} t}{d_p^2}\right) \quad (15)$$

where  $\bar{q}$ , the average concentration of mercury inside the particle, is defined by:

$$\bar{q} = \frac{3}{r_c^3} \int_0^{r_c} q r^2 dr \quad (16)$$

and  $m_t$  and  $m_\infty$  are the uptakes of mercury at time  $t$  and  $t = \infty$ . When the fractional uptakes,  $m_t/m_\infty$ , are larger than 70%, the following simplified equation can be used:

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \exp\left(-\frac{4\pi^2 D_{Hg} t}{d_p^2}\right) \quad (17)$$

For a particle size of  $d_p = 10 \mu\text{m}$ ,  $t = 3 \text{ s}$ , and 90% mercury uptake ( $m_t/m_\infty = 0.90$ ), the mercury diffusivity in activated carbon can be calculated using Equation (17):

$$D_{Hg} = -\frac{d_p^2}{4\pi^2 t} \ln\left(\frac{\pi^2}{6} \left(1 - \frac{m_t}{m_\infty}\right)\right) = -\frac{(10 \times 10^{-4})^2}{4 \times \pi^2 \times 3} \ln\left(\frac{\pi^2}{6} \times 0.1\right) = 1.52 \times 10^{-8} \text{ cm}^2/\text{s} \quad (18)$$

This value of diffusivity is in the range of configurational diffusion. The above calculations indicate that with a  $10 \mu\text{m}$  activated carbon particle, the intraparticle diffusion will be important only when the pore diameter is about  $3 \text{ \AA}$ , i.e., the molecular diameter of mercury.

It should be noted that in the above calculations it was assumed that the mercury concentration at the external surface of the particle remains constant. In the actual process, however, the mercury concentration in the flue gas decreases as the particles flow along the duct. If other conditions remain same, the diffusivity calculated under this situation is  $1.32 \times 10^{-8} \text{ cm}^2/\text{s}$  which is comparable to the value calculated using Equation (17).

From the above calculations, it can be concluded that intraparticle diffusion is unlikely to be the controlling step in the carbon injection process so long as the micropore size of the activated carbon is larger than around  $3 \text{ \AA}$ , which is true for most of activated carbon.

## DISCUSSION

Assuming that the adsorption of mercury from flue gas is mass transfer limited provides an indication of the maximum mercury efficiency possible for a specific amount of sorbent injected or an indication of the minimum amount of sorbent needed to achieve a specific mercury removal efficiency. The analysis presented in this paper indicates that under certain carbon injection conditions, mercury removal from coal-fired flue gas is film mass transfer controlled. For example,

Miller et al.<sup>5</sup> used a C/Hg ratio greater than 3000 for an activated carbon with a weight-averaged particle size of 5.5  $\mu\text{m}$ , to remove about 90% mercury from a flue gas. In the same study, for an iodine-impregnated activated carbon with a weight-averaged particle size of 3  $\mu\text{m}$ , the C/Hg ratio was about 1000. Such C/Hg ratios are comparable to those listed in Table 1.

Full-scale tests of carbon injection process in MSW flue gas also confirm the results shown in Table 1. Licata et al.<sup>9</sup> reported that the equilibrium mercury capacity of an activated carbon used in their tests was about 0.33 gHg/gAC which corresponds to a C/Hg ratio of 3 (temperature was not mentioned). However, in full-scale MSW tests with the same carbon, a C/Hg ratio of more than 300 was used to reduce mercury concentration in the flue gas from 600 to 70  $\mu\text{g}/\text{Nm}^3$  at 135 °C. This ratio corresponds to 0.0033 gHg/gAC which is only 1% of the equilibrium capacity of the carbon. In still another field test, White et al.<sup>10</sup> found that carbon injection methods (dry or wet) had a significant effect on the mercury removal while the type and surface chemistry of the activated carbon had not. These data suggested that mass transfer was controlling the mercury removal.

For conditions where mercury adsorption is mass transfer limited, measures should be taken to increase the mercury mass flux (from the bulk gas to the surface of carbon) rather than using a carbon with high capacity. To increase the mass transfer, either the mass transfer coefficient,  $k_p$ , or the interfacial area,  $a/V$ , should be increased. According to equation (3) the mass transfer coefficient increases with decreasing carbon particle size. Reducing carbon particle size also increases the interfacial area, without increasing carbon dosage. The most effective way to reduce the C/Hg ratio is therefore to decrease the carbon particle size. This is clearly shown in Table 1; when the carbon particle size is reduced from 10  $\mu\text{m}$  to 1  $\mu\text{m}$ , the C/Hg ratio is reduced from 13,611 to about 136.

Mass transfer limits only apply when the carbon has sufficiently high reactivity and capacity. When the operating temperature of the process is high, e.g. >180 °C, and the level of mercury removal is high, e.g. 95%, then the mercury capacity of carbon may become limiting. In this case, significantly larger amounts of carbon may be needed unless better carbon (larger capacity and high reactivity) can be produced.

## CONCLUSIONS

- The minimum amount of carbon needed to achieve a specific mercury removal efficiency via sorbent injection can be predicted by assuming mass transfer limitations.
- Mercury removal effectiveness can be increased by decreasing the size of the carbon injected, increasing the residence time, or the amount of carbon injected.
- Intraparticle diffusion is not important because of the small carbon sizes normally used for injection.
- If mercury removal is limited by the reactivity and capacity of the carbon (i.e. not mass transfer limited), then significantly more carbon than predicted by mass transfer limitations may be needed for effective mercury removal unless the reactivity and capacity of the carbon can be improved through structural and surface chemistry changes.

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